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Sterically congested phosphonium borate acids as effective Brønsted acid catalysts

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Dedicated to Martin Bennett on the occasion of his 80th birthday.

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ABSTRACT

Phosphonium borate acids $[HPPh_2(C_6F_5)][B(C_6F_5)_4]$ (**2**), $[HPMes_2(C_6F_5)][B(C_6F_5)_4]$ (**3**) and $[HPMes(C_6F_5)_2][B(C_6F_5)_4]$ (**4**) were synthesized via heterolytic dihydrogen cleavage in the presence of triisopropylsilylium and characterized by spectroscopic and crystallographic methods. Brønsted acid catalysis using compounds **2**–**4** proved to be efficient for a number of challenging reactions (namely ionic hydrogenation, hydroamination and hydroarylation), owing to the restrained nucleophilicity of the sterically hindered conjugate bases. Reactivity of compounds **2**–**4** suggests that their pK_a values are similar to that of diethyl oxonium acid.

1. Introduction

Brønsted acid catalysis has undergone tremendous advancement over the previous 20 years. Intrinsic to the mechanism of Brønsted acid catalysis, the role of the conjugate base must be considered. In the field of Brønsted acid asymmetric catalysis, the role of the conjugate base is pivotal to enantiomeric selectivity [1–3], whereas interaction with the conjugate base has been minimalized in the field of 'super-acidity'[4]. Essential to the development of 'super-acids', conjugate bases that are of very low basicity but stable in highly acidic environments have been developed [5–9]. However, such acids are widely incompatible with most organic reaction conditions, with their ability to protonate even weakly basic solvents, the electrochemical potential of the proton quickly adopts that of protonated solvent [10–12]. We sought to decouple the potential interaction between protonated reaction substrates and conjugate bases in Brønsted acid catalyzed reactions, so that our conjugate bases are reduced in role to 'proton carriers'. Additionally, we hoped to develop relatively strong Brønsted acids, allowing a wide range of challenging transformations to be catalysed. To achieve this, we looked for inspiration in developments in Frustrated Lewis Pair chemistry, where interaction between Lewis acids and bases is reduced using steric interactions. Thus our target acids are designed to act as proton sources, readily donating a coordinated proton, but having minimal interaction with larger acids after deprotonation occurs.

The unique unquenched reactivity of FLPs has been successfully utilized for the activation of small molecules, most notable being the reversible heterolytic cleavage of dihydrogen into protic and hydridic components. Such systems have shown tremendous application in the catalytic hydrogenation of imines, silyl enol ethers and olefins (inter alia) [13–16]. Generally, the use of electron rich Lewis bases to stabilise the evolved proton has limited the ability of FLP systems to catalyse the reduction of less basic substrates. However, Grimme and Paradies recently reported a phosphine-borane based FLP catalyst system employing the Lewis acid $B(C_6F_5)_3$ and electron poor phosphines {viz. $PPh_2(C_6F_5)$, $P(2,6\text{-}C_6H_3Cl_2)_3$ and $P(C_{10}H_7)_3$} capable of hydrogenating olefins using molecular hydrogen [17]. The high acidity of the intermediate phosphium acids, generated from H_2 cleavage, was key to the reactivity observed. However, instability of the intermediate phosphonium acids (in respect to recombination with $[HB(C_6F_5)_3]^-$) did not allow their isolation.

We reasoned that if such phosphonium acids were able to protonate olefins, and not bind bulky Lewis acids strongly, their isolation and modification to be even more hindered may provide convenient catalysts for a range of Brønsted acid catalyzed reactions. Herein we report the synthesis of new triaryl phosphine based Brønsted acids with their applications in catalyzing several organic transformations.

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2. Experimental

2.1. General information

All reactions, unless stated otherwise, were carried out in an inert atmosphere using standard Schlenk and high vacuum techniques. All common reagents used were obtained from commercial suppliers without further purification. Ether free $Li[B(C_6F_5)_4]$ [18], $[Ph_3C][B(C_6F_5)_4]$ [19], $PBr(C_6F_5)_2$ [20] and $PBrMes_2$ [21] were synthesized using previously reported procedures. All solvents used for reactions were either obtained from a Pure Solv MD-7 solvent purification system or dried following literature methods [22]. All deuterated solvents used were obtained from commercial sources and dried using calcium hydride followed by vacuum distillation. NMR spectra were recorded using Bruker Avance 500 (AV500) and Bruker Avance 400 (DRX400) NMR spectrometers. Gas Chromatography-Mass Spectrometry (GC–MS) results were recorded using an Agilent 5975 GCMSD with a HP-5 column (low resolution quadrupole benchtop mass spectrometer), coupled to an Agilent 7890A Gas Chromatograph. Known compounds were identified using the NIST Mass Spectra Library available in the GC–MS and by their reported ^{1}H NMR data.

2.2. X-ray crystallography

Single crystal data were measured on a four circles goniometer Kappa geometry Bruker AXS D8 Venture equipped with a Photon 100 CMOS active pixel sensor detector using a molybdenum (λ = 0.71073 Å) or copper (λ = 1.54180 Å) monochromatized X-ray radiation source.

Frames were integrated with the Bruker SAINT [23] software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method implanted in the software (Twinabs) [24]. The structures were solved by the direct method using the SHELXT program or SIR92 program [25]. Refinement of the structure was carried out by least squares procedures on weighted F^2 values using the SHELXL-version 2014/6 or using CRYSTALS [26,27]. All heavy atoms were assigned anisotropic displacement parameters, hydrogens atoms were located on difference Fourier maps then introduced as fixed or located geometrically. Compound **2** was found to be twinned, two distinct domains were depicted using the software Cell_now integrated in package software: APEX v2014.11.0. [28] The structure although twinned could be solved and fully refined.

2.3. Synthesis of phosphines

2.3.1. Dimesityl(pentafluorophenyl)phosphine

A freshly prepared ethereal solution (50 mL) of bromo(pentafluorophenyl)magnesium (prepared from 58 mmol of magnesium and 7.2 mL of bromopentafluorobenzene) was added dropwise to an ethereal solution (50 mL) of equimolar amount of bromodimesitylphosphine (13.32 g, 58 mmol) maintained in an ice-salt bath. After complete addition the reaction mixture was allowed to warm to room temperature and stirred overnight. $MgBr_2$ was separated by cannula filtration and the reaction was quenched with water (20 mL). The organic components were extracted with ether (3 × 30 mL) and combined extracts were reduced under vacuum. The crude mixture was purified by column chromatography to afford the title phosphine as a white solid. Yield: 12.0 g, 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (d, J = 4.0 Hz, 4H), 2.27 (s, 6H), 2.17 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): ^{13}C NMR (100.6 MHz, C_6D_6): δ 147.77 (dm, $^1J_{C-F}$ = 249.9 Hz, *C*F), 143.02 (d, $^1J_{C-}$P = 18.6 Hz, *C*P), 141.55 (dm, $^1J_{C-F}$ = 254.4 Hz, *C*F), 137.79 (dm, $^1J_{C-F}$ = 252.5 Hz, *C*F), 131.62 (d, J = 7 Hz), 130.65 (d, J = 4 Hz), 130.32 (d, J = 7 Hz), 114.10–113.45 (m, *ipso*-C), 22.80 (d, J = 17 Hz, *o*-*C*H$_3$), 20.89 (s, *p*-*C*H$_3$); ^{31}P NMR (162 MHz, $CDCl_3$): δ −47.91 (t, J = 37.0 Hz, 1P); ^{19}F NMR (376 MHz, $CDCl_3$): δ −129.46 to −129.78 (m, 2F), −153.03 (t, J = 20.5, 1F), −161.47 (td, J = 23.9, 8.9, 2F).

2.3.2. Mesityl-bis(pentafluorphenyl)phosphine

A freshly prepared tetrahydrofuran solution (50 mL) of bromomesitylmagnesium (prepared from 13.3 mmol of magnesium and 2.04 mL of bromomesitylene) was added dropwise to an ethereal solution (50 mL) of $PBr(C_6F_5)_2$ (2 mL, 13.3 mmol) maintained at below 0 °C. The resulting cloudy mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue stirred vigorously with dry methanol for five minutes before evaporation. The cycle of methanol addition and solvent removal was performed three times. The resulting solid residue was dissolved in dry diethyl ether (50 mL) and separated from $MgBr_2$ by cannula filtration. The solvent was evaporated and the residue dried under vacuum for 12 h at room temperature. The crude mixture was purified by recrystallization from dry methanol. Yield: 3.5 g, 55%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 (d, J = 4.0 Hz, 2H), 2.40 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.10 (dm, $^1J_{C-F}$ = 246.8 Hz, *C*F), 145.05 (d, $^1J_{C-}$P = 20.8 Hz, *C*P), 141.96 (d, J = 1.4 Hz), 141.79 (dm, $^1J_{C-F}$ = 254.6 Hz, *C*F), 137.67 (dm, $^1J_{C-F}$ = 255.7 Hz, *C*F), 130.12 (d, J = 6 Hz), 122.76 (d, J = 14 Hz), 109.45–108.61 (m, *ipso*-C), 22.86 (d, J = 19 Hz, *o*-*C*H$_3$), 21.28 (s, *p*-*C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ −54.71 (q, J = 29 Hz, 1P); ^{19}F NMR (376 MHz, $CDCl_3$) δ −131.28 to −131.52 (m, 4H), −151.71 (td, J = 20.5, 1.0, 2H), −160.73 (m, 4H).

2.4. Synthesis of phosphonium salts

2.4.1. Method I

Ether free $Li[B(C_6F_5)_4]$ (0.69 g, 1.0 mmol) and phosphine (1.0 mmol) were dissolved in dichloromethane. The solution was saturated with hydrogen chloride by passing HCl gas through the solution for five minutes. The reaction vessel was sealed and the mixture was allowed to stir for 24 h. Resulting mixture was filtered and the colourless filtrate was concentrated under reduced pressure. Hexane was added to induce precipitation. The resulting white solid was washed with hexane and dried in vacuo.

2.4.2. Method II

A flame dried Teflon capped Schlenk tube was charged with 0.92 g of $[Ph_3C][B(C_6F_5)_4]$ (1.0 mmol) and 2.0 mL of chlorobenzene. An excess amount of triisopropylsilane (0.25 mL, 1.22 mmol) was added to the solution which was stirred at room temperature for 10 min. A chlorobenzene solution of triaryl phosphine (1.0 mmol) was added to the mixture. After 10 min, an aliquot was taken to confirm the formation of **1** {^{31}P NMR (202 MHz): δ −9.95 (s, 1P). ^{29}Si NMR (99 MHz): δ 38.61 (d, Si, J = 22 Hz).}. In the cases of $PMes_2(C_6F_5)$ and $PMes(C_6F_5)_2$, NMR data showed the silylium/phosphine mixture to be a Frustrated Lewis Pair. The reaction tube was immersed into liquid nitrogen to freeze the solution. The tube was exposed to vacuum and refilled with hydrogen gas. The reaction vessel was sealed and the mixture was heated overnight at 60 °C. The resulting pale brown solution was concentrated under reduced pressure. The remaining solution was triturated with hexane, yielding a pale brown precipitate which was isolated and thoroughly washed with hexane before being dried under vacuum.

2.4.3. Diphenyl(pentafluorophenyl)phosphonium tetrakis (perfluorophenyl)borate (*2*)

Off white solid. Yield: 0.72 g (70%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.27 (d, 1H, J = 528 Hz, P–*H*), 7.41–7.36 (m, 2H, C_{Ar}-*H*), 7.24–8.19 (m, 4H, C_{Ar}-*H*), 7.13–7.07 (dd, 4H, J = 16, 7.6 Hz, C_{Ar}-*H*); ^{31}P NMR

(161.9 MHz, C_6D_6): δ −12.84 (s, 1P); ^{11}B NMR (128 MHz, C_6D_6): δ −16.32; ^{19}F NMR (376 MHz, C_6D_6) δ −126.79 to −126.86 (m, 2F), −132.66 (br, s, BAr^F), −133.84 to −133.65 (m, 1F), −153.45 to −153.55 (dd, J = 28, 11.6 Hz, 2F), −162.93 (t, J = 20 Hz, BAr^F), −167.04 (t, J = 17.6 Hz, BAr^F); ^{13}C NMR (125 MHz, C_6D_6): δ 149.00 (dbr, $^1J_{C-F}$ = 239 Hz, *C*F), 148.81 (dbr, $^1J_{C-F}$ = 261 Hz, *C*F), 138.90 (dbr, $^1J_{C-F}$ = 244 Hz, *C*F), 137.77 (d, J = 3 Hz), 137.03 (dbr, $^1J_{C-F}$ = 244 Hz, *C*F), 133.62 (d, J = 13 Hz), 132.00 (d, J = 11.6 Hz), 131.45 (d, J = 14.6 Hz), 131.07 (d, J = 13.8 Hz), 130.11, 128.88, 125.45–124.24 (m).

2.4.4. Dimesityl(pentafluorophenyl)phosphonium tetrakis (perfluorophenyl)borate (**3**)

Off white solid. Yield: 0.88 g (78%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.23–7.96 (d, 1H, J = 508 Hz, P–*H*), 7.19 (d, 4H, J = 8 Hz, C_{Ar}-*H*), 2.41 (s, 6H, *CH*$_3$), 2.28 (s, 12H, *CH*$_3$); ^{31}P NMR (161.9 MHz, CD_2Cl_2): δ −38.00 (br, 1P); ^{11}B NMR (128 MHz, CD_2Cl_2): δ −16.66; ^{19}F NMR (376 MHz, CD_2Cl_2) δ −127.57 (br, 2F), −133.11 (br, 8F, BAr^F), −135.15 (m, 1F), −153.57 (br, 2F), −163.84 (t, 4F, J = 22.5 Hz, BAr^F), −167.70 (t, 8F, J = 20 Hz, BAr^F); ^{13}C NMR (125 MHz, CD2Cl2): δ 149.58 (d, J = 3 Hz), 147.57 (dm, $^1J_{C-F}$ = 231 Hz, *C*F), 144.16 (d, J = 11.7 Hz), 140.58 (dm, $^1J_{C-F}$ = 238 Hz, *C*F), 139.39 (dm, $^1J_{C-F}$ = 266 Hz, *C*F), 136.70 (dm, $^1J_{C-F}$ = 244 Hz, *C*F), 133.26 (d, J = 12.5 Hz), 107.02 (d, J = 87.7 Hz), 22.99 (d, J = 10 Hz, *o*-*C*H$_3$), 20.89 (d, J = 1.25, *p*-*C*H$_3$). HRMS-ESI (*m*/*z*): calcd. for $[C_{21}H_{23}F_5P_1]^+$ 437.1458; observed 437.1453.

2.4.5. Mesityl-bis(pentafluorphenyl)phosphonium tetrakis (perfluorophenyl)borate (**4**)

Off white solid. Yield: 0.65 g (75%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.66–8.31 (d, 1H, J = 540 Hz, P–*H*), 7.275 (d, 2H, J = 4 Hz, C_{Ar}-*H*), 2.48 (s, 6H, *CH*$_3$), 2.45 (s, 3H, *CH*$_3$); ^{31}P NMR (161.9 MHz, CD_2Cl_2): δ −44.24 (br, 1P); ^{11}B NMR (128 MHz, CD_2Cl_2): δ −16.68; ^{19}F NMR (376 MHz, CD_2Cl_2) δ −127.11 to −127.30 (m, 4F), −131.65 to −131.81 (m, 2F), −133.43 (m, BAr^F), −152.40 to −152.51 (m, 4F), −163.62 (t, J = 22, BAr^F), −167.68 (t, J = 15, BAr^F); ^{13}C NMR (125 MHz, CD2Cl2): δ 152.13 (d, J = 2.7 Hz), 148.55 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 145.24 (d, J = 13 Hz), 139.52 (dm, $^1J_{C-F}$ = 252 Hz, *C*F), 138.66 (dm, $^1J_{C-F}$ = 243 Hz, *C*F), 136.73 (dm, $^1J_{C-F}$ = 240.4 Hz, *C*F), 133.29 (d, J = 13 Hz), 130.28 (d, J = 5.7 Hz), 128.93, 102.23 (d, J = 93 Hz), 101.53 (d, J = 92 Hz), 22.41 (d, J = 11 Hz, *o*-*C*H$_3$), 22.03 (d, J = 1 Hz, *p*-*C*H$_3$). HRMS was not possible due to the highly acidic nature of the phosphonium.

2.4.6. General experimental procedure for the hydrogenation reaction

A reaction tube with a Teflon cap was charged with equimolar (0.1 mmol) amounts of olefin and triisopropylsilane. A dichloromethane solution of 10 mol% catalyst was added to the tube and the mixture was heated at 50 °C for 18 h. The reaction mixture was taken in volumetric flask and diluted with DCM. The diluted solution was analysed by GC–MS.

2.4.7. General experimental procedure for the hydroamination reaction

In a Glove box a reaction tube with a Teflon cap was charged with 0.1 mmol of olefin and fivefold excess of aryl amine. A dichlorobenzene solution of 10 mol% catalyst was added to the tube and the mixture was heated at 135 °C for 48 h. The reaction mixture was taken in volumetric flask and diluted with DCM. The diluted solution was analysed by GC–MS.

2.4.8. General experimental procedure for the hydroarylation reaction

In a Glove box a Teflon capped reaction tube was charged with 0.1 mmol of olefin and fivefold excess of aryl amine. A dichloromethane solution of 10 mol% catalyst was added to the tube and the mixture was heated at 50 °C for 18 h. The reaction mixture was taken in volumetric flask and diluted with DCM. The diluted solution was analysed by GC–MS.

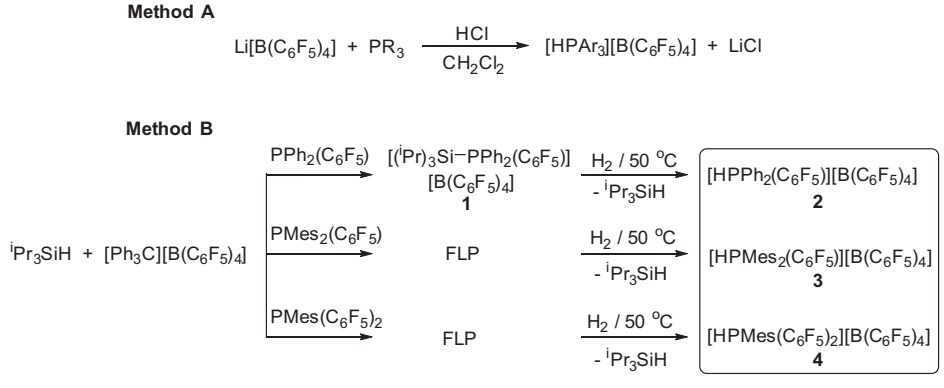
3. Results and discussion

3.1. Synthesis of phosphonium borates **2**, **3** and **4**

The syntheses of triaryl phosphine based Brønsted acids $[HPAr_3][B(C_6F_5)_4]$ (Ar = Phenyl, Mesityl, pentafluorophenyl) was achieved by passing dry hydrogen chloride gas through a dichloromethane solution of phosphine and $Li[B(C_6F_5)_4]$ (Scheme 1, Method A). This method suffers from a severe drawback that in presence of trace diethyl ether, electron poor phosphines compete for protonation with ether. In cases of comparable basicity, oxonium/phosphonium mixtures in benzene could be purified in the presence of excess phosphine under Dean–Stark distillation conditions. However, purification of phosphoniums much more acidic than diethyl oxonium remained impossible using this technique.

Consequently, our focus turned to dihydrogen cleavage using FLP reactivity. In an effort to isolate the *in situ* generated phosphonium acid, we employed silylium (R_3Si^+) based Lewis acids. Phosphine-silylium pairs have previously been shown to activate dihydrogen with basic phoshines [29–31].

Room temperature treatment of ^{i}Pr$_3$SiH with $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene and subsequent addition of diphenyl(pentafluorophenyl)phosphine afforded the classical donor–acceptor complex $[^i Pr_3Si–PPh_2(C_6F_5)][B(C_6F_5)_4]$ (**1**) (Scheme 1, Method B). Appearance of a doublet at δ 38.61 (J = 22 Hz) in the ^{29}Si NMR spectrum and a downfield shift of the phosphorus resonance in the ^{31}P NMR spectrum by $\Delta\delta$ 14.55 to −9.85 ppm as compared to the



Scheme 1. Synthesis of phosphonium salts in acidic medium. Method A: salt metathesis between HCl and $Li[B(C_6F_5)_4]$ in the presence of phosphine; Method B: H_2 activation by a silylium/phosphine FLP.

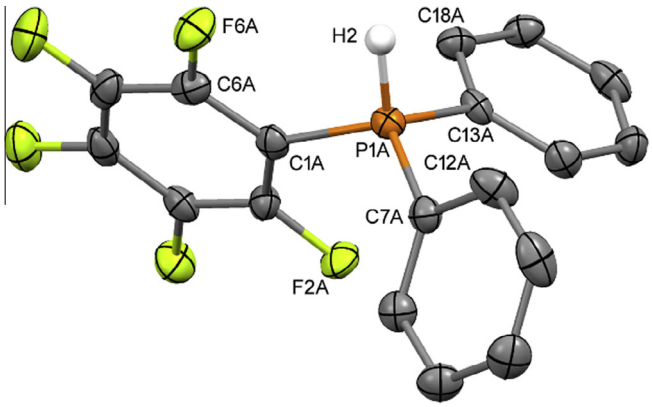


Fig. 1. Structure (50% probability thermal ellipsoids) of the cationic unit in **2** with selected atoms labelled. Hydrogen atoms except H2 are omitted for the sake of clarity. Selected bond distances and angles are listed in Table 1.

corresponding free phosphine (−24.41 ppm) was indicative of the adduct formation [31]. Adduct **1** reacted with molecular hydrogen at 50 °C (4 atm) with concomitant formation of $^{i}Pr_3SiH$ and the borate salt of the corresponding phosphonium, $[HPPh_2(C_6F_5)][B(C_6F_5)_4]$ (**2**) in high yield (Scheme 1, Method B).

The ^{1}H NMR spectrum of **2** exhibits a doublet at δ 7.27 with a large H–P coupling (J_{P-H} = 528 Hz) and the ^{31}P NMR signal shifts upfield from δ −9.85 (**1**) to δ −12.84 (**2**). These data are in agreement with the closely related ion pair $[HPPh_2(C_6F_5)][HB(C_6F_5)_3]$ reported by Grimme and Paradies [17]. The molecular structure of **2** was established by X-ray crystallography. The structure of the phosphonium moiety may be considered as pseudo tetrahedral with the central phosphorus atom subtended by one proton, one perfluorophenyl and two phenyl groups (Fig. 1). All P–C bond distances are marginally shorter as compared to the parent phosphine [32]. The bond length shortening may be attributed to the increased electronegativity of the phosphorus atom due to protonation. The shortening of P–C bond lengths is often observed when a phosphine is protonated [33]. It is also observed that the $\angle C_{Ar}$–P–C_{Ar} angle becomes larger in the protonated phosphine (Table 1).

Evidently, the formation of adduct **1** is indicative that the conjugate base $PPh_2(C_6F_5)$ is not as inert as intended. Thus, bulkier phosphines $PMes_2(C_6F_5)$ and $PMes(C_6F_5)_2$ were prepared. These phosphines form corresponding FLPs with $[^{i}Pr_3Si][B(C_6F_5)_4]$, instead of classical donor–acceptor complexes. When hydrogen gas (4 atm) is introduced and the reaction vessel is heated at 50 °C, these FLPs also cleave H_2 to generate silane and the corresponding phosphonium salts $[HPMes_2(C_6F_5)][B(C_6F_5)_4]$ (**3**) and $[HPMes(C_6F_5)_2][B(C_6F_5)_4]$ (**4**). Downfield shifts of the ^{31}P NMR signals (δ −38.00 ppm for **3** and δ −44.24 ppm for **4**) and appearance of doublets with large phosphorus to hydrogen coupling constants (J = 504 Hz for **3** and J = 540 for **4**) in the ^{1}H NMR spectrum were observed for the phosphonium salts. All these phosphonium salts were fully characterized by spectroscopic methods and X-ray crystallography (Fig. 2). Table 1 compares the structural metrics of phosphonium salts **2**, **3** and **4**, and data collection and refinement details are listed in Table 2. Phosphine bound hydrogen atoms were located in a fourier difference map and refined isotropically. Although P–H distances in compounds **2**–**4** are indistinguishable (i.e. within e.s.u.), their J_{P-H} values increase with the presence of more electron withdrawing groups. This phenomenon can be extended to the observation that trialkyl phosphonium J_{P-H} values are documented to be even smaller than those observed in compounds **2**, **3** and **4** [34,35], in agreement with Bent's rule [36].

3.2. Hydrogenation of olefins

The phosphonium salts show immense potential as strong Brønsted acids, with deprotonation of **4** with an equivalent of

Table 1
Select structural metrics for compounds **2**, **3** and **4**.

	Compound **2**	Compound **3**	Compound **4**
P–H distance (Å)	P1A–H2: 1.31(6)	P1–H1: 1.30(2)	P1–H1: 1.38(5)
P–$C_{Mes/Ph}$ distance (Å)	P1A–C7A: 1.777(5) P1A–C12A: 1.781(5)	P1–C7: 1.787(2) P1–C13: 1.789(2)	P1–C1: 1.779(6)
P–C_{ArF} distance (Å)	P1–C1A: 1.795(6)	P1–C1: 1.803(2)	P1–C10: 1.794(6) P1–C16: 1.795(6)
C–P–C angles (°)	C1A–P1A–C7A: 116.0(2) C7A–P1A–C13A: 110.8(2) C13A–P1A–C1A:107.1(2)	C1–P1–C7: 111.49(10) C7–P1–C13: 114.04(10) C13–P1–C1: 116.85(10)	C1–P1–C10: 110.7(3) C10–P1–C16: 113.1(3) C16–P1–C1: 116.1(3)

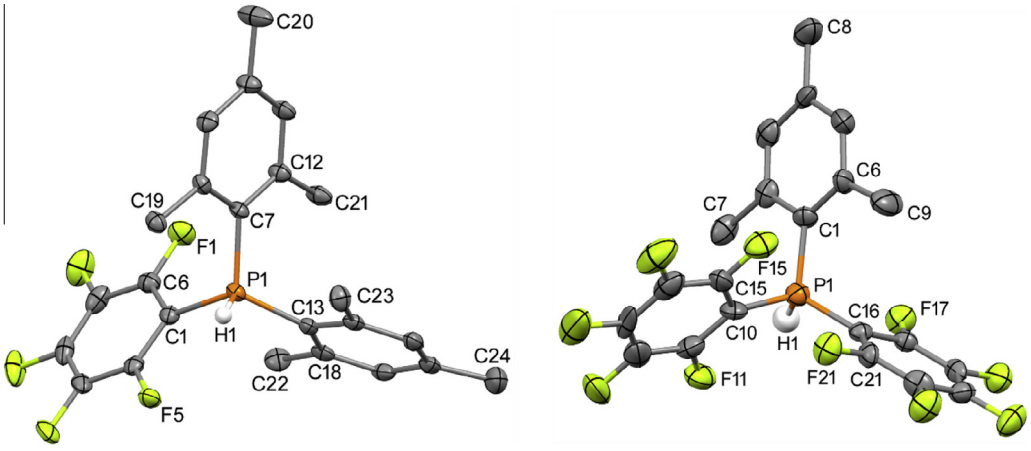
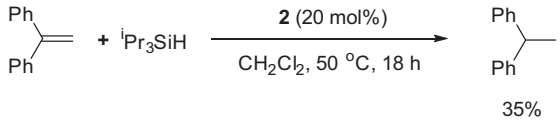


Fig. 2. Structure (50% probability thermal ellipsoids) of the cationic unit in **3** (left) and **4** (right) with select atoms labelled. Hydrogen atoms except H1 are omitted for the sake of clarity. Selected bond distances and angles are listed in Table 1.

Table 2
Crystal data collection and refinement details for compounds **2**, **3** and **4**.

	Compound **2**	Compound **3**	Compound **4**
Formula	$C_{42}H_{11}B_1F_{25}P_1$	$C_{48}H_{21}B_1F_{25}P_1$	$C_{45}H_{12}B_1F_{30}P_1$
Formula weight	1032.28	1114.43	1164.31
T (K)	100(2)	100(2)	200(2)
λ (Å)	1.54180	0.71073	1.54180
Crystal system	orthorhombic	triclinic	monoclinic
Space group	P c a 21 (No. 29)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	16.3144(15)	11.0701(11)	10.8557(7)
b (Å)	10.7191(10)	13.7688(17)	15.8832(12)
c (Å)	42.595(4)	15.811(2)	24.6736(12)
α (°)	90	66.624(4)	90
β (°)	90	85.890(4)	93.066(3)
γ (°)	90	81.913(4)	90
V (Å^3)	7448.8(12)	2189.8(5)	4248.2(5)
Z	4	2	4
ρ_{calc} (g/cm^3)	1.841	1.690	1.820
μ (mm^{-1})	2.165	0.207	2.158
F(000)	4064	1108	2288
θ range for data collection (°)	4.124–74.641	2.309–28.285	3.310–64.771
Index ranges	$-20 \leqslant h \leqslant 15$ $-13 \leqslant k \leqslant 13$ $-53 \leqslant l \leqslant 52$	$-13 \leqslant h \leqslant 14$ $-18 \leqslant k \leqslant 18$ $-21 \leqslant l \leqslant 21$	$-12 \leqslant h \leqslant 12$ $0 \leqslant k \leqslant 18$ $0 \leqslant l \leqslant 28$
Reflections collected	57753	22411	24178
Independent reflections	13984	10373	7079
Completeness to θ (%)	99.9	96.8	98.2
Restraints/parameters	1/1251	0/686	0/698
Goodness-of-fit (GOF) on F^2	1.063	0.996	0.904
Final R indices [$I > 2\sigma(I)$]	0.0462	0.0624	0.0802
R indices (all data)	0.0469	0.1421	0.1411
Largest diff. in peak and hole (e Å^{-3})	1.38 and −0.44	0.84 and −0.38	0.81 and −0.92



Scheme 2. Catalytic hydrogenation of olefin using the Brønsted acid **2**.

diethyl ether suggesting a pK_a *ca* −2 or lower for **4**. Indeed, Paradies and co-workers have measured the pK_a of $[HPPh_2(C_6F_5)]^+$ in MeCN and demonstrated that it can catalyze the ionic hydrogenation of olefins in the presence of the hydride donor $[HB(C_6F_5)_3]^-$, generated *in situ* by H_2 cleavage with $PPh_2(C_6F_5)$ and $B(C_6F_5)_3$ [17,37]. Similarly, hydrosilanes are known as hydride donors and extensively used as reducing agents. Ionic hydrogenation using excess mixtures of Brønsted acid/hydrosilane was pioneered by Kurasanov and co-workers, who used CH_3COOH and Et_3SiH for the hydrogenation of ketones, olefins and imines [38,39].

Thus, triarylphosphonium salts and $^iPr_3SiH$ were tested for the ionic hydrogenation of olefins. In a test reaction, an equimolar mixture of 1,1′-diphenylethylene and $^iPr_3SiH$ was treated with 0.2 equivalents of **2** in dichloromethane (DCM) at 50 °C (Scheme 2). Overnight heating resulted in the full consumption of olefin, but the reaction suffers from side reactions (such as hydrosilylation of the olefin and the hydroarylation – Friedel–Crafts alkylation – of the aryl groups of both olefin and the catalyst) effectively reducing the hydrogenated product yield (35% yield). In an attempt to alleviate side-reactivity, catalysts **3** and **4** were tested under identical conditions to **2**. Use of the phosphonium salt **3** for the ionic hydrogenation of 1,1′-diphenylethylene afforded clean conversions to the desired product, but the presence of two mesityl groups renders the phosphonium salt less acidic than **2**, thus catalytic activity was much reduced resulting in poor conversion. Phosphonium **4** was found to be a very good hydrogenation catalyst, allowing the use of 10 mol% catalyst loading. Thus, when a dichloromethane solution of the catalyst **4** (10 mol%) was treated with and an equimolar mixture of 1,1′-diphenylethylene and $^iPr_3SiH$ then heated overnight (∼18 h) at 50 °C, quantitative consumption of the olefin was observed with a 94% product yield (Entry 1, Table 3).

In contrast to previously reported ionic hydrogenations where stoichiometric measures of both acid and hydride are required, the inertness of our conjugate base allows residual water, present in our solvent, to preferentially react with silyium by-product and generate Brønsted acid and siloxane/silanol. Thus the reaction can be considered the phosphonium catalyzed reduction of olefin by water and silane.

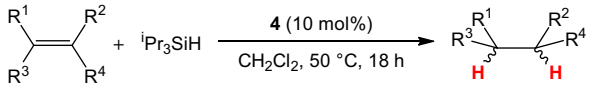
It was found that the non-aromatic, aprotic solvent DCM afforded higher conversion compared to aromatic solvents benzene, toluene, chlorobenzene and 1,2-dichlorobenzene. Use of toluene leads to high amounts of Friedel–Crafts hydroarylation side-products. Several olefins were screened to evaluate the performance of catalyst **4** in ionic hydrogenation (Table 1).

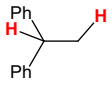
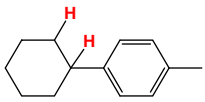
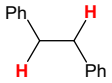
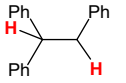
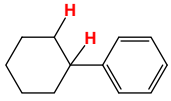
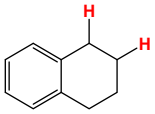
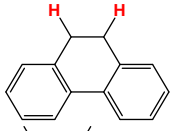
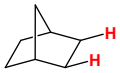
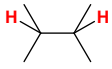
3.3. Hydroamination of olefins

Although several transition metal based catalysts have been extensively used for the addition of amines to alkenes [40,41], Brønsted acids have been underinvestigated until recently. In 2002 Hartwig reported the intramolecular amination of aminoalkenes catalyzed by triflic acid and sulfuric acid [42,43]. Later, Bergman reported divergent hydroamination/hydroarylation reactivity of activated alkenes with anilines using $[NH_3Ph][B(C_6F_5)_4]$ as catalyst [44]. Intrigued by the success of ammonium salts as hydroamination catalysts we employed the phosphonium borate salts **3** and **4** for catalysing hydroamination reaction of aniline and activated olefin.

For direct comparison, we chose substrates closely related to those employed by Bergman et al. in their initial report for acid catalysed hydroamination/hydroarylation. We found that our yields and product distributions mirrored those obtained by Bergman et al. employing an anilinium borate acid source, their most

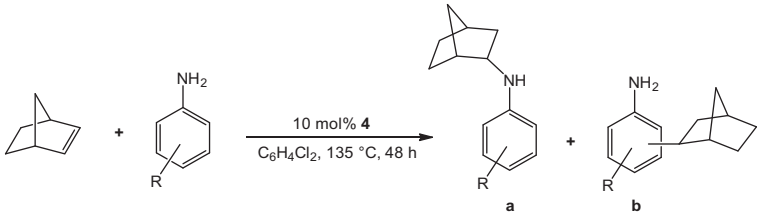
Table 3
Ionic hydrogenation of olefins by $^{i}Pr_3SiH$ and H_2O catalysed by compound **4**.



Entry	Product	Product yield (%)[b]	Entry	Product	Product yield (%)[b]
1		>90	6		75
2		5	7[a]		79
3		>90	8		>90
4		17	9		26
5		27			

[a] Reaction conducted at room temperature.
[b] Yield determined by ^{1}H NMR and/or GC–MS.

Table 4
Hydroamination of norbornene catalysed by compounds **3** and **4**.



Entry	*R* group	Product yield (%)[a] (**a**:**b**)
1	H	80 (35:45)
2	1,2,3,4,5-F_5	87 (87:0)[b]
3	4-OMe	66 (24:42)
4	2,4,6-Me_3	72 (60:12)
5	4-CF_3	88 (56:32)
6	2,4,6-F_3	56 (54:2)
7	4-F	93 (60:33)

[a] Yield determined by ^{1}H NMR and/or GC–MS.
[b] Catalyst **3** employed.

active catalyst. However, in contrast to anilinium, our catalyst proved immune to reaction with olefins and did thus not result in unwanted side-products.

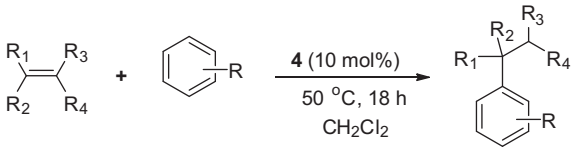
In our preliminary experiments we used aniline and pentaflurophenyl aniline with norbornene. Reaction of norbornene with aromatic amines in presence of 10 mol% of both catalysts afforded a mixture of hydroaminated and hydroarylated products as evident from the GC–MS (Table 4).

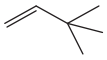
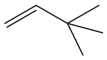
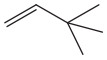
3.4. Hydroarylation of olefins

Given the ability of **4** to catalyse hydroarylation of aryl amines, the hydroarylation of a range or arenes was attempted. A number of metal complexes have been reported to catalyse olefin hydroarylation [45–50]. However, the simplicity and high activity of Brønsted acid catalyzed hydroarylations make Brønsted acids an attractive choice for alkylation of arenes [51–53]. The use of strong acids and/or drastic reaction conditions often limits the applicability and functional group tolerance of many Brønsted acid catalysed olefin hydroarylations. This can be due in part to both the activity of the Lewis acidic carbocation generated and the nature of the conjugate base. In this respect, it was hoped that catalysts **2**–**4** may allow evaluation of the reaction without any interference from the hindered conjugate bases.

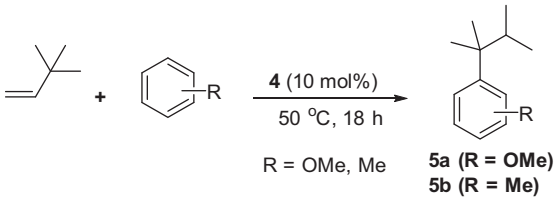
Friedel–Crafts alkylations under catalytic conditions (10 mol%) using olefins that proceeded via tertiary or cyclic carbocations produced a mixture of expected *ortho*-, *meta*- and *para*-products in high conversion and yield (Table 5). However, when 3,3-dimethyl-1-butene was employed as the olefin, carbocation rearrangement was observed and 1,1,2-trimethylpropyl hydroarylated products **5a-d** were recovered in high yield (Scheme 3).

Table 5
Hydroarylation of olefins catalysed by compound **4**.



Entry	Arene	Olefin	Product Yield (%)[a] (*ortho:meta:para*)
1	Anisole		92(0:0:92)[b]
2			90 (24:21:55)
3			58 (21:11:26)
4			100 (33:0:67)
6	Toluene		95 (23:0:72)[c]
7			100 (32:17:51)
8			99 (32:17:50)
9			58 (26:0:32)
10	Mesitylene		<5
11			66
12			6
13			<5

[a] Yield determined by ^{1}H NMR and/or GC–MS.
[b] Rearrangement to **5a**.
[c] Rearrangement to **5b**.



Scheme 3. Hydroarylation of anisole with 3,3-dimethyl-1-butene catalyzed by **4**.

Employing the olefin 2,3-methyl-2-butene to access compounds **5a** and **5b** provided a change in yields and product distributions, suggesting that rearrangement of 3,3-dimethyl-1-butene may occur after electrophilic attack of the arene. Friedel–Crafts alklyations that strongly disfavoured *meta*-addition (*viz.* 3,3-dimethyl-1-butene, cyclooctene and 2,3-dimethyl-2-butene) provided very poor yields when reacted with mesitylene.

4. Conclusions

Compounds **2**–**4** have been shown to be sufficiently acidic to initiate a number of Brønsted acid catalysed reactions. The conjugate base phosphines of compounds **2**–**4**, generated upon deprotonation, were shown to have minimal impact on ionic hydrogenation, hydroamination and hydroarylation reactions. These acids may serve a particularly useful role in situations where oxo-acids are not tolerated (e.g. protolysis of hard metal Lewis acids) [54].

Acknowledgments

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Appendix A. Supplementary data

CCDC 1472071, 1472072 and 1472073 contains the supplementary crystallographic data for **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.05.049.

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